

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B41M 5/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/07558</b> <b>(43) International Publication Date:</b> 18 February 1999 (18.02.99)
<b>(21) International Application Number:</b> PCT/US97/22653 <b>(22) International Filing Date:</b> 11 December 1997 (11.12.97) <b>(30) Priority Data:</b> 08/909,021 11 August 1997 (11.08.97) US <b>(71) Applicant:</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint-Paul, MN 55133-3427 (US). <b>(72) Inventors:</b> WARNER, David; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). SCHREADER, Loren, R.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). <b>(74) Agents:</b> HORNICKEL, John, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> COATED MICROPOROUS INKJET RECEPTIVE MEDIA AND METHOD FOR CONTROLLING DOT DIAMETER <b>(57) Abstract</b> <p>An inkjet receptor medium is disclosed wherein the medium is microporous and has on one major surface an imaging layer comprising a coating of a mixture of amorphous precipitated and fumed silicas and binder. Dot diameter of pigmented inkjet inks can be controlled using the receptor medium, which is advantageous for inks delivered in small picoliter volumes. Methods of making and using the medium are also disclosed.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**Coated Microporous Inkjet Receptive Media and  
Method for Controlling Dot Diameter**

**Field of Invention**

5                    This invention relates to inkjet receptive media that is coated in a manner that can control the spread of an ink droplet reaching the media to provide a superior image graphic.

**Background of Invention**

10                   Image graphics are omnipresent in modern life. Images and data that warn, educate, entertain, advertise, etc. are applied on a variety of interior and exterior, vertical and horizontal surfaces. Nonlimiting examples of image graphics range from advertisements on walls or sides of trucks, posters that advertise the arrival of a new movie, warning signs near the edges of stairways.

15                   The use of thermal and piezo inkjet inks have greatly increased in recent years with accelerated development of inexpensive and efficient inkjet printers, ink delivery systems, and the like.

Thermal inkjet hardware is commercially available from a number of multinational companies, including without limitation, Hewlett-Packard Corporation of Palo Alto, CA, USA; Encad Corporation of San Diego, CA, USA; Xerox Corporation of Rochester, NY, USA; LaserMaster Corporation of Eden Prairie, MN, USA; and Mimaki Engineering Co., Ltd. of Tokyo, Japan. The number and variety of printers changes rapidly as printer makers are constantly improving their products for consumers. Printers are made both in desk-top size and wide format size depending on the size of the finished image graphic desired. Nonlimiting examples of popular commercial scale thermal inkjet printers are Encad's NovaJet Pro printers and H-P's 650C, 750C, and 2500CP printers. Nonlimiting examples of popular wide format thermal inkjet printers include H-P's DesignJet printers, where the 2500CP is preferred because it has 600X600 dots/inch (dpi) resolution with a drop size in the vicinity of about 40 picoliters.

20  
25  
30

3M markets Graphic Maker Inkjet software useful in converting digital images from the Internet, ClipArt, or Digital Camera sources into signals to thermal inkjet printers to print such image graphics.

Inkjet inks are also commercially available from a number of multinational companies, particularly 3M which markets its Series 8551; 8552; 8553; and 8554 pigmented inkjet inks. The use of four principal colors: cyan, magenta, yellow, and black (generally abbreviated "CMYK") permit the formation of as many as 256 colors or more in the digital image.

Media for inkjet printers are also undergoing accelerated development. Because inkjet imaging techniques have become vastly popular in commercial and consumer applications, the ability to use a personal computer to print a color image on paper or other receptor media has extended from dye-based inks to pigment-based inks. And the media must accommodate that change. Pigment-based inks provide more durable images because pigment particles are contained in a dispersion before being dispensed using a thermal inkjet print head.

Inkjet printers have come into general use for wide-format electronic printing for applications such as, engineering and architectural drawings. Because of the simplicity of operation and economy of inkjet printers, this image process holds a superior growth potential promise for the printing industry to produce wide format, image on demand, presentation quality graphics.

Therefore, the components of an inkjet system used for making graphics can be grouped into three major categories:

- 1 Computer, software, printer.
- 2 Ink.
- 3 Receptor medium.

The computer, software, and printer will control the size, number and placement of the ink drops and will transport the receptor medium through the printer. The ink will contain the colorant which forms the image and carrier for that colorant. The receptor medium provides the repository which accepts and holds the ink. The quality of the inkjet image is a function of the total system.

However, the composition and interaction between the ink and receptor medium is most important in an inkjet system.

Image quality is what the viewing public and paying customers will want and demand to see. From the producer of the image graphic, many other  
5 obscure demands are also placed on the inkjet media/ink system from the print shop. Also, exposure to the environment can place additional demands on the media and ink (depending on the application of the graphic).

Current inkjet receptor media are direct coated with a dual layer receptor according to the disclosure contained in PCT International Patent  
10 Publication WO97/17207 (Warner et al.) and are marketed by 3M under the brands 3M™ Scotchcal™ Opaque Imaging Media 3657-10 and 3M™ Scotchcal™ Translucent Imaging Media 3637-20.

Inkjet inks are typically wholly or partially water-based, such as disclosed in U.S. Pat. No. 5,271,765. Typical receptors for these inks are plain  
15 papers or preferably specialist inkjet receptor papers which are treated or coated to improve their receptor properties or the quality of the images resulting therefrom, such as disclosed in U.S. Pat. No. 5,213,873.

Many inkjet receptor compositions suitable for coating onto plastics to make them inkjet receptive have been disclosed. Applications for overhead  
20 transparencies are known in the art. These are composed of transparent plastic materials such as polyester, which alone will not accept the aqueous inks and are therefore coated with receptor layers. Typically these receptor layers are composed of mixtures of water soluble polymers which can absorb the aqueous mixture from which the inkjet ink comprises. Very common are hydrophilic layers comprising  
25 poly(vinyl pyrrolidone) or poly(vinyl alcohol), as exemplified by U. S. Pat. Nos. 4,379,804; 4,903,041; and 4,904,519. Also known are methods of crosslinking hydrophilic polymers in the receptor layers as disclosed in U.S. Pat. Nos. 4,649,064; 5,141,797; 5,023,129; 5,208,092; and 5,212,008. Other coating compositions contain water-absorbing particulates such as inorganic oxides, as  
30 disclosed in U.S. Pat. Nos. 5,084,338; 5,023,129; and 5,002,825. Similar properties

are found for inkjet paper receptor coatings, which also contain particulates, such as corn starch as disclosed in U.S. Pat. No. 4,935,307 and 5,302,437.

The disadvantage that many of these types of inkjet receptor media suffer for image graphics is that they comprise water-sensitive polymer layers.

5 Even if subsequently overlaminated still contain a water-soluble or water-swella-  
ble layer. This water-sensitive layer can be subject over time to extraction with water  
and can lead to damage of the graphic and liftoff of the overlaminate.

Additionally, some of the common constituents of these hydrophilic coatings  
contain water-soluble polymers not ideally suitable to the heat and UV exposures  
10 experienced in exterior environments, thus limiting their exterior durability.  
Finally, the drying rate after printing of these materials appears slow since until  
dry, the coating is plasticized or even partially dissolved by the ink solvents  
(mainly water) so that the image can be easily damaged and can be tacky before it  
is dry.

15 In recent years increasing interest has been shown in microporous  
films as inkjet receptors to address some or all of the above disadvantages. If the  
film is absorbant to the ink, after printing the ink absorbs into the film itself into  
the pores by capillary action and feels dry very quickly because the ink is away  
from the surface of the printed graphic. The film need not necessarily contain  
20 water-soluble or water swella-  
ble polymers, so potentially could be heat and UV  
resistant and need not be subject to water damage.

Porous films are not necessarily receptive to water-based inkjet if  
the material is inherently hydrophobic and methods of making them hydrophilic  
have been exemplified e.g. by PCT Publication WO 92/07899.

25 Other films are inherently aqueous ink absorptive because of the  
film material, e.g. Teslin™ (a silica-filled polyolefin microporous film) available  
from PPG Industries and of the type exemplified in U.S. Pat. No. 4,861,644.  
Possible issues with this type of material are that if used with dye based inks image  
density can be low depending on how much of the colorant remains inside the  
30 pores after drying. One way of avoiding this is to fuse the film following printing  
as exemplified in PCT Publication WO 92/07899.

Other methods are to coat the microporous film with a receptor layer as disclosed in U.S. Pat. No. 5,605,750.

As stated above, the relationship between the ink and the media is key to image graphic quality. With printers now reaching 600X600 dpi precision, inkjet drop size is smaller than in the past. As stated previously, a typical drop size for this dpi precision, is about 40 picoliters, which is one-third the size of prior drop sizes of 140 picoliters used in wide format inkjet printers. Printer makers are striving for even smaller drop sizes, e.g., 10-20 picoliters. With pigmented inkjet inks, drop size determines the quantity of pigment particles that reside in each drop and are to be directed to a predetermined area of media.

When the inkjet ink drop contacts the receptor medium, a combination of two things occur. The inkjet drop diffuses vertically into the medium and diffuses horizontally along the receptor surface, with a resulting spread of the dot.

However, with pigment-based inkjet inks of the right particle size and if used with a film of the right pore-size, some filtration of the colorant is possible at the surface of the film resulting in a good density and color saturation. However, images can still be very poor if dot-gain is low due to "banding phenomena" where insufficient ink remains to generate the appropriate halftone image. If dot-size is too small, then errors due to media advancement or failed printhead nozzles can cause banding. This problem would not be seen with larger drop size printers because larger dots could cover up prior printing errors. However, if dots are too large, then edge acuity is lost. Edge acuity is a reason for increased dpi image precision. Ability to control dot diameter is therefore an important property in an inkjet receptor medium.

U.S. Pat. No. 5,605,750 exemplifies a pseudo-boehmite coating applied to the silica-filled microporous film such as Teslin™. The coating contains alumina particles of pseudo-boehmite of pore radius 10 to 80 Å. Also disclosed is an additional protective layer of hydroxypropylmethyl cellulose.

30

#### Summary of Invention

This invention has utility for the production of graphics using wide-format inkjet printers and pigment-based ink. This invention solves the problem of banding in fine precision inkjet printing systems by controlling the dot diameter of a small inkjet drop on an inkjet receptor medium.

5           One aspect of the invention is an inkjet receptor medium comprising a microporous medium having on one major surface an imaging layer comprising a coating of amorphous precipitated silica and binder. The binder is preferably a water-based ethylene-acrylic acid dispersion, and other organic liquids. The coating also preferably comprises a mixture of amorphous precipitated and fumed  
10   silicas.

          The imaging layer is constructed applying a range of weight ratio of silica to binder and applied in a range of coating weights such that the dried layer is capable of controlling the dot diameter of pigmented inkjet inks. Specifically, the dot diameter of pigment particles in a single inkjet drop can be controlled to  
15   minimize undesired banding of ink on the inkjet receptor medium.

          Using the present invention as compared with the substrate with no imaging layer, one can increase dot diameter for different color inks by controlling the silica/binder weight ratio.

          Another aspect of the invention is a method of coating an imaging  
20   layer on a microporous medium, wherein the layer comprises a coating of a mixture of amorphous precipitated and fumed silicas and binder, in order to form an inkjet receptor medium; and printing an inkjet ink drop on the inkjet receptor medium wherein a dot formed on the medium, containing pigment particles gains in size on the imaging layer.

25           A feature of the invention is the retention of pigment particles at or near the imaging surface of the receptor medium while allowing carrier liquids of the ink to be transported through the microporous medium.

          Another feature of the invention is the interaction of the imaging  
30   layer with the pigment particles in the ink to enhance the appearance of dot diameter with a minimal drop size currently available.



An advantage of the invention is the ability to maximize the appearance of a minimal drop size by impelling the dot on the receptor medium to spread horizontally along the medium while the carrier liquid is impelled to drain vertically through the medium. Using the medium of the present invention, one can take a drop of minimal volume and maximize the usage of pigment particles to be seen in the image, without adversely affecting visual acuity. Without control of dot diameter, pigment particles "stack up" where deposited on the medium. With dot diameter control of the present invention, one can control the spread of pigment particles over a larger area of the medium's imaging surface, without loss of visual acuity.

Another advantage of the invention is ability to minimize errors in the appearance of an image graphic where the printer and ink employ maximum dpi currently available.

Other features and advantages will be explained in relation to the following embodiments of the invention.

#### Embodiments of the Invention

##### Microporous Material

The inkjet receptive medium begins with microporous film or membrane that has an imaging major surface and an opposing major surface. The material is preferably hydrophilic and capable of transporting carrier liquids in ink away from the imaging major surface.

Microporous membranes are available with a variety of pore sizes, compositions, thicknesses, and void volumes. Microporous membranes suitable for this invention preferably have adequate void volume to fully absorb the inkjet ink discharged onto the hydrophilic layer of the inkjet recording medium. It should be noted that this void volume must be accessible to the inkjet ink. In other words, a microporous membrane without channels connecting the voided areas to the imaging surface coating and to each other (i.e., a closed cell film) will not provide the advantages of this invention and will instead function similarly to a film having no voids at all.

Void volume is defined in ASTM D792 as the  $(1 - \text{Bulk density} / \text{Polymer density}) * 100$ . If the density of the polymer is not known, the void volume can be determined by saturating the membrane with a liquid of known density and comparing the weight of the saturated membrane with the weight of the membrane prior to saturation. Typical void volumes for hydrophilic, microporous, polymeric membrane range from 10 to 99 percent, with common ranges being 20 to 90%.

Void volume combined with membrane thickness determines the ink volume capacity of the membrane. Membrane thickness also affects the flexibility, durability, and dimensional stability of the membrane. Membrane can have a thickness ranging from about 0.01 mm to about 0.6 mm (0.5 mil to about 30 mils) or more for typical uses. Preferably, the thicknesses are from about .04mm to about .25mm (about 2 mils to about 10 mils).

The liquid volume of typical inkjet printers is approximately 40 to 150 picoliters per drop, although it is contemplated that printers will eventually have drop sizes of 10-20 picoliters, which should also benefit from this invention. Thus, this invention is useful for drop sizes of less than 150 picoliters. Typical resolution is 118 to 283 drops per centimeter. High resolution printers supply smaller dot volumes. Actual results indicate a deposited volume of 1.95 to 2.23 microliters per square centimeter with each color. Solid coverage in multicolor systems could lead to as high as 300% coverage (using undercolor removal) thus leading to volume deposition of 5.85 to 6.69 microliters per square centimeter.

Hydrophilic, microporous, polymeric membrane has a pore size that is less than the nominal drop size of the inkjet printer in which the inkjet recording medium is to be used. The pore size may be from 0.01 to 10 micrometers with a preferred range of from 0.5 to 5 micrometers with pores on at least one side of the sheet.

The porosity, or voided aspect, of membrane need not go through the entire thickness of the membrane, but only to a sufficient depth to create the necessary void volume. Therefore, the membrane may be asymmetric in nature, such that one side possesses the aforementioned properties, and the other side may

be more or less porous or non-porous. In such a case, the porous side must have adequate void volume to absorb the liquid in the ink that is passed through the imaging layer.

Nonlimiting examples of hydrophilic, microporous, polymeric membranes include polyolefins, polyesters, polyvinyl halides, and acrylics with a micro-voided structure. Preferred among these candidates are a microporous membrane commercially available as "Teslin" from PPG Industries as defined in U.S. Pat. No. 4,833,172 and hydrophilic microporous membranes typically used for microfiltration, printing or liquid barrier films as described in U.S. Pat. Nos. 4,867,881, 4,613,441, 5,238,618, and 5,443,727. Teslin microporous membrane has an overall thickness of approximately 0.18 mm, and the void volume has been measured experimentally to be 65.9%. The ink volume capacity of the membrane is thus 11.7 microliters per square centimeter. Therefore, this membrane has sufficient void volume combined with thickness to fully absorb the ink deposited by most inkjet printers, even at 300% coverage, without considering the amount retained in the hygroscopic layer.

Membrane can optionally also include a variety of additives known to those skilled in the art. Nonlimiting examples include fillers such as silica, talc, calcium carbonate, titanium dioxide, or other polymer inclusions. It can further include modifiers to improve coating characteristics, surface tension, surface finish, and hardness.

Membrane can be used as commercially provided or calendered. Calendering of the membrane can be performed using conventional material handling equipment and pressures such that calendering results in a calendered medium that has higher gloss after calendering as opposed to before calendering. It is acceptable to calender the medium such that the 85° gloss measurement is between about 15 units and 35 units as measured on a Byk-Gardner Gloss Meter, and preferably between about 20 units and about 35 units. It is preferred to calender the membrane after coating with the imaging layer, although it is possible to calender prior to the membrane being coated.

### Imaging Layer

The imaging layer comprises a binder and amorphous precipitated silica, and preferably a mixture of at least a binder and amorphous precipitated and fumed silicas.

5           The weight percent ratio of silica to binder can range from about 3.5:1 to about 2:1 and preferably from about 3.0:1 to about 2.25:1. The preferred range has been found to maximize dot diameter without harming visual acuity for the image graphic printed on the receptor medium.

10           The coating weight (dried on the microporous medium) can range from about 10 to about 300 mg/ft<sup>2</sup> (108 to 3300 mg/m<sup>2</sup>) and preferably from about 30 to about 200 mg/ft<sup>2</sup> (330 to 2200 mg/m<sup>2</sup>). The preferred range has been found to maximize dot diameter without harming visual acuity.

15           The binder can be any polymer from water-based or organic solvent-based systems that can be coated onto the microporous material and can adhere to the material with the silica particles contained therein. . Preferably, the binder is water-resistant, yet can be coated from a water-based dispersion. Nonlimiting examples of such binders include ethylene-acrylic acid copolymers and their salts, styrene-acrylic acid copolymers and their salts, and other (meth)acrylic moiety containing polymers. Preferably, the binder is a water-based  
20   ethylene-acrylic acid dispersion commercially available as Michem Prime 4983R resin from Michelman Inc., 9080 Shell Road, Cincinnati, OH 45236-1299).

25           The binder retains silicas in the imaging layer. Silicas have been found to interact with pigment particles in the ink and any dispersants associated with the pigment particles. Silicas useful in the invention include amorphous precipitated silicas alone or in mixture with fumed silicas.

30           Such silicas have typical primary particle sizes ranging from about 15 nm to about 6  $\mu$ m. These particle sizes have great range, because two different types of silicas are useful in the present invention. The optional fumed silicas have a much smaller particle size than the amorphous precipitated silicas and typically constitute the lesser proportion of the mixture of silicas when both are present. Generally when both are present in the mixture, the weight ratio of silicas

(amorphous:fumed) ranges greater than about 1:1 and preferably greater than about 3:1.

Amorphous precipitated silicas are commercially available such sources as FK-310 silicas from Degussa Corporation of Ridgefield Park, NJ, USA.

5 Fumed silicas are commercially available as Cab-o-sil silicas from Cabot Corp. of Tuscola, IL, USA and Aerosil MOX 170 silicas from Degussa Corporation of Ridgefield Park, NJ, USA.

Control of dot diameter can be obtained by variation of the silica/binder weight ratio. As compared with a control of substrate without the  
10 imaging layer thereon, and by varying the silica to binder weight percent ratio from about 2.0:1 to about 3.5:1, one can increase dot diameter in a range from about 32% to about 83% for cyan ink; about 55% to about 104% for magenta ink; about 29% to about 48% for yellow ink; and about 35% to about 90% for black ink. The variation of increase depends on ink formulations as well as the silica to binder  
15 weight ratio. But one skilled in the art will appreciate the versatility and utility of adjustments in silica/binder weight ratio to achieve the advantages of the present invention.

#### Optional Adhesive Layer and Optional Release Liner

20 The receptor medium optionally but preferably has an adhesive layer on the opposite major surface of the microporous material that is also optionally but preferably protected by a release liner. After imaging, the receptor medium can be adhered to a horizontal or vertical, interior or exterior surface to warn, educate, entertain, advertise, etc.

25 The choice of adhesive and release liner depends on usage desired for the image graphic.

Pressure sensitive adhesives can be any conventional pressure sensitive adhesive that adheres to both membrane and to the surface of the item upon which the inkjet receptor medium having the permanent, precise image is  
30 destined to be placed. Pressure sensitive adhesives are generally described in Satas, Ed., Handbook of Pressure Sensitive Adhesives 2nd Ed. (Von Nostrand

Reinhold 1989). Pressure sensitive adhesives are commercially available from a number of sources. Particularly preferred are acrylate pressure sensitive adhesives commercially available from Minnesota Mining and Manufacturing Company of St. Paul, Minnesota and generally described in U.S. Pat. Nos. 5,141,790, 5 4,605,592, 5,045,386, and 5,229,207 and EPO Patent Publication EP 0 570 515 B1 (Steelman et al.).

Release liners are also well known and commercially available from a number of sources. Nonlimiting examples of release liners include silicone coated kraft paper, silicone coated polyethylene coated paper, silicone coated or 10 non-coated polymeric materials such as polyethylene or polypropylene, as well as the aforementioned base materials coated with polymeric release agents such as silicone urea, urethanes, and long chain alkyl acrylates, such as defined in U.S. Pat. No. 3,957,724; 4,567,073; 4,313,988; 3,997,702; 4,614,667; 5,202,190; and 5,290,615; and those liners commercially available as Polyslik brand liners from 15 Rexam Release of Oakbrook, IL, USA and EXHERE brand liners from P.H. Glatfelter Company of Spring Grove, PA, USA.

#### Method of Making the Imaging Layer

Coating can be carried out using dispersions of between 0.5% and 20 6% approximately solids at a 0.002 inch (0.051 mm) wet gap on a knife (notch bar) coater or equivalent (e.g. at 3 mil (0.76 mm) between 0.3% and 4% etc.) or using gravure coating onto either Teslin™ film, or constructions containing Teslin™ such as Teslin/adhesive/release liner laminates which can be assembled using adhesives and lamination or coating procedures known in the art. Preferably, to 25 avoid foaming during coating up to 12.5% of a solvent such as methyl ethyl ketone can be added to solutions between 1.0 and 1.4% solids.

In one embodiment of the method, one can construct the receptor medium from coating adhesive on a release liner, laminating the microporous material, coating and calendaring the imaging layer.

30 In another embodiment of the method, one can laminate the microporous material on an adhesive on a transfer liner and then transfer to the

final release liner either before or after calendering and either before or after coating on the imaging layer.

Preferably, the order of assembly is the first embodiment.

5                    Usefulness of the Invention

Inkjet receptor media of the present invention can be employed in any environment where inkjet images are desired to be precise, stable, and rapid drying. Commercial graphic applications include opaque signs and banners.

10                   Inkjet recording media of the present invention have dimensional stability, after calendering, as measured by hygroscopic expansion of less than 1.5% size change in all directions with a relative humidity change from 10% relative humidity to 90% relative humidity. As such, the media of the present invention are preferred over coated papers because the paper is apt to change shape or dimension during processing or during use.

15                   Inkjet receptor media of the present invention can accept a variety of inkjet ink formulations to produce rapid drying and precise inkjet images. The thickness and composition of the individual layers of the inkjet recording medium can be varied for optimum results, depending on several factors, such as: ink droplet volume; ink liquid carrier composition; ink type (pigment or blend of  
20                   pigment and dye); and manufacturing technique (machine speed, resolution, roller configuration); etc.

Commonly, inkjet ink formulations have pigments in water blended with other solvents. Both water and the other solvents carry the pigments into the imaging layer and then continue into membrane for rapid drying of the image in  
25                   the imaging layer to form the precise image.

The imaging layer of the present invention has been found to control dot diameter over a range of silica/binder weight ratios and dried coating weight range disclosed above. Surprisingly, it has been found that dot diameter can reach a peak of up to about 150  $\mu\text{m}$  on a printer that delivers drop volumes of  
30                   about 40 picoliters at 600 dpi when the weight percent ratio of silica/binder is about 2.75:1 and the dried coating weight is about 130  $\text{mg}/\text{ft}^2$  (1430  $\text{mg}/\text{m}^2$ ).

Variation of either parameter substantially in either direction will reduce the amount of dot diameter. One skilled in art can employ any possible combination of the acceptable ratios and dried coating weights to control dot diameter to minimize banding or undesirable imaging defects.

5                   For example, one can increase the silica/binder ratio to about 3:1 and reduce the dried coating weight to about 32 mg/ft<sup>2</sup> (352 mg/m<sup>2</sup>) to achieve dot diameter that is about 75-92% less than the peak dot diameter, the range depending on which color of ink is employed. .

10                   For example, one can reduce the silica/binder ratio to about 2:1 and the dried coating weight remains the same to achieve dot diameter that is about the same as at the peak dot diameter but has less visual acuity. .

15                   Drying can be measured as the time required before the image becomes tack free or does not smear when lightly rubbed. Typically, the image feels dry within about 2 minutes and preferably within about 30 seconds after imaging. The use of the imaging layer to provide dot diameter and the use of the microporous medium to provide quick drying of the image are advantages combined in the receptor medium of the invention not previously found in the art.

20                   Dot size, and hence dot diameter relative to an uncoated microporous material, can be measured using a Jenavert optical microscope at 625 times magnification with a graduated eyepiece. The eyepiece had previously been calibrated for microns image size per eyepiece graduated division. Dots as near circular as possible can be selected, and three dots per color being measured along orthogonal axes for dot diameter. All six diameters per dot color can be averaged to find the final diameter for that color dot.

25                   Dot diameter can range from about 70 to about 150  $\mu$ m and preferably from about 80 to about 120  $\mu$ m for each printing color in order to minimize banding. Using an imaging layer according to the present invention, this goal can be achieved even when printing drops as small as 40 picoliters in volume.

30                   The formation of precise inkjet images is provided by a variety of commercially available printing techniques. Nonlimiting examples include thermal inkjet printers such as DeskJet brand, PaintJet brand, Deskwriter brand,



DesignJet brand, and other printers commercially available from Hewlett Packard Corporation of Palo Alto, California. Also included are piezo type inkjet printers such as those from Seiko-Epson, spray jet printers and continuous inkjet printers. Any of these commercially available printing techniques introduce the ink in a jet spray of a specific image into the medium of the present invention. Drying is much more rapid under the present invention than if the imaging layer were to be applied to a similar non-porous media.

The media of the present invention can be used with a variety of inkjet inks obtainable from a variety of commercial sources. It should be understood that each of these inks have different formulations, even for different colors within the same ink family. The effect of controlling dot diameter according to the present invention can have varying results among various ink formulations, even within different colors. Therefore, some inks may require this method of the present invention more than others. Nonlimiting sources include Minnesota Mining and Manufacturing Company, Encad Corporation, Hewlett Packard Corporation, and like. These inks are preferably designed to work with the inkjet printers described immediately above and in the background section above, although the specifications of the printers and the inks will have to be reviewed for appropriate drop volumes and dpi in order to further refine the usefulness of the present invention. For example, banding issues can be addressed well in "40 picoliter" printers using the present invention. However, there could be other issues addressed in "larger drop volume" printers using the present invention. Because a feature of the present invention is the ability to control drop diameter, the ability to tailor specific media for specific inks and specific printers is achievable.

The following examples further disclose embodiments of the invention.

#### Examples

R is defined as the ratio of total weight of silica to resin in the dry coating.

30

#### **Example 1 - Preparation of Imaging Layer**

Stock solution of premix paste at 22% solids

To a beaker was added Michem Prime 4983R (58.90g) available from Michelman Inc., 9080 Shell Road, Cincinnati, OH 45236-1299). Deionized water was added (14.99g) and the dispersion stirred. To the stirred water-based dispersion was added ethanol (46.61g). After mixing for a short time the dispersion was vigorously mixed and fumed silica Aerosil MOX 170 (9.53g) and amorphous precipitated silica FK-310 (30.97g) added in that order (both silicas available from Degussa Corporation, 65 Challenger Road, Ridgefield Park, NJ).

The mixture was homogenized using a Silverson high-speed Multi-Purpose Lab mixer, fitted with a Disintegrating Head for five minutes.

The 22% premix paste was diluted with successive dilutions of an equal weight of ethanol-water mix (38g deionized water to 12g ethanol) to get solutions of the following percent solids: 5.5%, 2.75%, 1.375% and 0.6875%. To avoid settling of the silica which would alter the results (by altering the binder to silica ratio) the solutions need to be coated immediately.

**Example 2 - Preparation of a Variety of Silica/Binder Formulations**

The following formulations at 11% solids in the table were made up as described in example 1. They were diluted one part by weight solution to one part by weight solvent mix (38g deionized water, 12g ethanol) and coated immediately.

TABLE 1: Formulations with varying R ratio

R	Michem Prime 4983R	Silica MOX 170	Silica FK 310	Ethanol	Water	Total
2	36.8135	4.331	14.07573333	53.1881	142.591667	251
2.25	33.98169231	4.497576923	14.61710769	53.1881	144.715523	251
2.5	31.55442857	4.640357143	15.08114286	53.1881	146.535971	251
2.75	29.4508	4.7641	15.48330667	53.1881	148.113693	251
3	27.610125	4.872375	15.8352	53.1881	149.4942	251
3.25	25.986	4.967911765	16.14569412	53.1881	150.712294	251
3.5	24.54233333	5.052833333	16.42168889	53.1881	151.795044	251

Thus a series of coating solutions at 5.5% solids with varying R ratios was produced. This was coated onto 7293 label stock (available from 3M Industrial and Converter Systems Division of 3M, 3M Center, Maplewood, MN 55144-1000), a label stock comprising Teslin™ SP 700, and adhesive and a liner. However, it is  
5 believed the same results are obtained if coated onto Teslin™ SP without adhesive or liner. The samples had varying R ratios but the same approximate coating weight.

The invention is not limited to the above embodiments. The claims follow.

What is claimed is:-

1. An inkjet receptor medium, comprising:  
a microporous medium having on one major surface an imaging  
5 layer comprising a coating of amorphous precipitated silica and binder.
2. The medium of Claim 1, wherein the binder comprises a water-  
based ethylene-acrylic acid dispersion, and wherein the imaging layer further  
comprises fumed silica.  
10
3. The medium of Claims 1 or 2, wherein the silica and binder are  
present in a percent weight ratio ranging from about 3.5:1 to about 2:1 and wherein  
the imaging layer can have a dried coating weight ranging from about 100 to about  
3300 mg/m<sup>2</sup>.  
15
4. The medium of any of Claims 1-3, wherein the imaging layer  
can have a dot diameter increase ranging from about 29 percent to about 104  
percent when printing an inkjet ink drop having a volume of about 40 picoliters.
- 20 5. The medium of any of Claims 1-4, further comprising a pressure  
sensitive adhesive layer on a major surface opposing the imaging layer.
6. The medium of any of Claims 1-5, wherein the medium is  
calendered and has a 85° gloss measurement greater than 15 units.  
25
7. The medium of any of Claims 1-6, wherein the imaging layer is  
water-resistant.
8. A method of controlling dot diameter on an inkjet receptor  
30 medium, comprising the steps of:

(a) coating an imaging layer on a microporous medium, wherein the layer comprises amorphous precipitated silica and binder, in order to form an inkjet receptor medium; and

(b) printing an inkjet ink drop on the inkjet receptor medium

5 wherein a dot formed on the medium, containing pigment particles gains in size on the imaging layer.

9. The method of Claim 8, wherein the binder comprises a water-based ethylene-acrylic acid dispersion and wherein the layer further comprises  
10 fumed silica and wherein the silica and binder are present in a percent weight ratio ranging from about 3.5:1 to about 2:1.

10. The method of Claim 8 or 9, wherein the imaging layer can have a dried coating weight ranging from about 100 to about 3300 mg/m<sup>2</sup> and  
15 wherein the imaging layer can have a dot diameter ranging from about 29 percent to about 104 percent when printing an inkjet ink drop having a volume of about 40 picoliters.

11. The method of any of Claims 8-10, further comprising before  
20 printing step (b), the step of calendering the inkjet receptor medium.

12. An inkjet image, comprising the steps of printing an inkjet ink on a medium of any of Claims 1-7, wherein the ink comprises pigment particles and is dispersed in drops of less than 150 picoliters in volume and wherein the  
25 pigment particles spread along the medium to a controlled amount, wherein the control in the medium is determined by a weight percent ratio of silica/binder and a dried coating weight of imaging layer on the medium.

# INTERNATIONAL SEARCH REPORT

Int. ional Application No

PCT/US 97/22653

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 033 (M-114), 27 February 1982 & JP 56 148583 A (CANON INC), 18 November 1981, see abstract	1-12
A	WO 97 22467 A (PPG INDUSTRIES INC) 26 June 1997 see page 1, line 3 - page 3, line 25 see page 19, line 3 - line 4	1,8,12
A	US 5 605 750 A (ROMANO CHARLES E ET AL) 25 February 1997 cited in the application see column 1, line 65 - column 2, line 16 see column 3, line 18 - column 14, line 46 ----- -/--	1,8,12



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 April 1998

Date of mailing of the international search report

28/04/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Markham, R

# INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 97/22653

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	<p>EP 0 810 086 A (OJI YUKA SYNT PAPER CO LTD) 3 December 1997</p> <p>see page 2, line 5 - line 10</p> <p>see page 3, line 7 - line 52</p> <p>see page 4, line 30 - page 6, line 2</p> <p>see page 7, line 10 - line 35</p> <p>see figures</p> <p>see examples</p>	1-12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/22653

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9722467 A	26-06-97	AU 1279697 A	14-07-97
US 5605750 A	25-02-97	GB 2308553 A	02-07-97
EP 0810086 A	03-12-97	JP 9325717 A	16-12-97